$$E_{hk}^{lm}(2) = E_h^l + E_k^m + (hh|kk) + (ll|mm) - (hh|mm)$$
$$- (ll|kk) - \tfrac{1}{2}((lh|lh) + (mk|mk)) - (hk|hk)$$
$$- (ml|ml) + \tfrac{3}{2}((hm|hm) + (kl|kl))$$
$$E_{hk}^{lm}(2)_{,0} = 3^{1/2}((hm|kl) - (hl|km)) \qquad (A25)$$

Appendix III

Given is the determinant of the following form:

$$\begin{vmatrix} E_0 - \epsilon & H_{10} & \cdot & \cdot & H_{n0} \\ H_{01} & E_1 - \epsilon & 0 & \cdot & 0 \\ \cdot & 0 & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot \\ H_{0n} & 0 & \cdot & \cdot & E_n - \epsilon \end{vmatrix} = 0 \quad (A31)$$

This determinant may be written as given by eq A32

$$\prod_{i=1}^{n} (E_i - \epsilon)\left((E_0 - \epsilon) - \sum_{i=1}^{n} (H_{0i}{}^2/(E_i - \epsilon))\right) = 0 \quad (A32)$$

As the product in eq A32 is not zero, we can simplify the expression and find by setting $E_0 = 0$ eq A33

$$\epsilon = -\sum_{i}^{n} (H_{0i}{}^2/(E_i - \epsilon)) \qquad (A33)$$

We start with the perturbational solution ϵ_0 for ϵ and find iteratively by the Newton interpolation formula

$$\epsilon_{j+1} = \frac{\sum_{i}^{n} (H_{0i}{}^2(E_i - \epsilon_j)^{-1} (\epsilon_j(H_{0i} - \epsilon_j)^{-1} + 1))}{\sum_{i}^{n} H_{0i}{}^2(E_i - \epsilon_j)^{-2} - 1} \qquad (A34)$$

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Ab Initio Calculation of Some Vertical Excitation Energies of N-Methylacetamide

Larry E. Nitzsche and Ernest R. Davidson*

Contribution from the Department of Chemistry, BG-10, University of Washington, Seattle, Washington 98195. Received March 24, 1978

Abstract: Ab initio SCF-CI calculations have been performed on several states of N-methylacetamide near the ground-state equilibrium geometry. The $^3\pi\pi^*$ state is predicted to lie about 0.5–0.6 eV above the $^3n\pi^*$ state. The $^3n\pi^*$ state is expected to lie about 0.2–0.3 eV below the experimental $^1n\pi^*$ state at 5.5 eV. The $^1\pi\pi^*$, $^1\pi3p_\pi$, and ^1n3p configurations are predicted to be strongly mixed, giving three states of large oscillator strength in the region of the broad V band of the absorption spectrum.

Introduction

The peptide bond is the principal link between amino acid residues in proteins. The role that excitation of the amide group plays in the properties of proteins is still much debated. It has been suggested that the amide chain might be semiconducting.[1]

This would require a relatively low excitation energy for the amide group. Such a low excitation energy could also lead to energy transfer between aromatic residues along the protein chain.

Evans and Gergely[2] carried out semiempirical band calculations which seemed to show that semiconduction was possi-
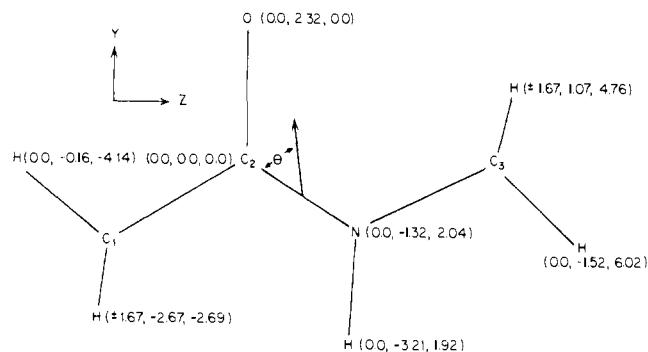
O (0,0, 2.32, 0,0)

Figure 1. *N*-Methylacetamide coordinates and axis system.

ble. On the basis of calculations on formamide and di- and tripeptides, the Pullmans have shown that such a low-energy band is unlikely.[1] McGlynn and co-workers,[3,4] however, have recently presented evidence that a low-energy state may exist in the free amide.

The absorption spectra of various methylated amides have been measured in the gas phase,[5] in various solvents, and in the neat liquid.[6] Sweigart and Turner[7] have studied the photoelectron spectra, and McGlynn and co-workers[4] have investigated the emissive properties. It is clear from these spectra that methylation produces large energy shifts. Consequently, the excited states of formamide, which have been widely studied theoretically,[1] may have little bearing on the peptide linkage.

McGlynn and co-workers[3] have emphasized the need for using *N*-methylacetamide (NMA) as the model compound. They have predicted that, unlike formamide, NMA will have a low-energy $^3\pi\pi^*$ state. Initially they believed this state would lie near 3 eV, based on the theoretical value of the $\pi\pi^*$ exchange integral calculated with ground-state SCF orbitals and on the observed position of the $^1\pi\pi^*$ excitation (the V band).[3] They have more recently raised their estimate[4] to 4.5 eV but, on the basis of the fact that the amides are nonemissive, still predict $^3\pi\pi^*$ to lie below $^3n\pi^*$.

Ab initio calculations of the type reported here produced results for formamide[8] and formaldehyde in close agreement with the experimental assignments[9] and with the calculations of Harding and Goddard.[8] The vertical excitation energies for formamide are about 5.8 eV ($^3\pi\pi^*$), 5.4 eV ($^3n\pi^*$), and 5.7 eV ($^1n\pi^*$). Calculations on the $^1\pi\pi^*$ state were less reliable because this state lies above ^1n3s and is nearly degenerate with the lowest ^1n3p state. Large differences in relaxation and correlation between these configurations make it difficult to predict the correct ordering of these states.[10]

Past theoretical calculations concerned with the barrier to rotation in the ground state of NMA are quite numerous. To our knowledge, no previous ab initio calculations have been reported on excitation energies. Semiempirical interpretations of the spectrum in terms of $n\pi^*$ and $\pi\pi^*$ valence states are, of course, quite common.

Procedure

The geometry used in all calculations was the assumed ground-state structure shown in Figure 1. All nonhydrogen bond lengths and angles were from a crystal structure.[11] The methyl hydrogen coordinates were found by assuming a C–H bond length of 1.091 Å and a H–C–H angle of 108°. The N–H bond length and angle were taken from formamide. The methyl groups were oriented to maintain a plane of symmetry and to have the orientation of the peptide linkage.

A Dunning[12] [5s, 3p] contraction of Huzinaga's[13] (9s, 5p) Cartesian Gaussian basis was used for the C_2, N, and O atoms.

A (4s) to [2s] contraction was used for the hydrogens, and a Dunning [4s, 2p] contraction was used for C_1 and C_3. No polarization functions were included. A (2s, 1p, 1d) uncontracted set of Rydberg orbitals with exponents suggested by Dunning and Hay[14] were centered on the carbonyl carbon. The valence part of this basis set is, hence, of slightly better than double-ζ quality and should be able to represent the small contractions and expansions of orbitals caused by charge shifts in excited states. The Rydberg orbitals are required to represent the low-lying 3s, 3p, and 3d states which are an order of magnitude more diffuse than any valence state.

This gave 67a' and 20a'' basis functions from which 16a' and 4a'' doubly occupied molecular orbitals were constructed in the ground-state Roothaan-SCF calculation. Our CI program is presently limited to 60 MO's so the virtual orbital basis was truncated. Improved virtual orbitals were found for the a'' space for a hole in 4a'' and for the a' space for a hole in 16a'. The set of MO's was then truncated to the 45a' and 15a'' orbitals of lowest orbital energy. These orbitals were used in calculations on the ground state, the $^2A'$ and $^2A''$ ion states, and excited $^1A'$ states.

Excited-state SCF calculations were performed for $^1n\pi^*$, $^3n\pi^*$, and $^3\pi\pi^*$. Canonical orbitals from the $^3n\pi^*$ state were truncated to 45a' and 15a'' for CI calculations on $^1n\pi^*$ and $^3n\pi^*$. Canonical orbitals from $^3\pi\pi^*$ were similarly truncated for the CI calculation on that state.

It was our intention to proceed with the $^1\pi\pi^*$ state using the nonorthogonal SCF procedure developed for formamide.[15] For NMA, however, all of the low-energy $^1\pi k\pi^*$ states gave a Rydberg $k\pi^*$ orbital, so no valence π^* orbital could be obtained. Thus it was not possible to define a V state SCF result. Consequently, the $^1A'$ manifold was calculated using ground state IVO's.

In an attempt to obtain a balanced description of the $^1A'$ states, all single and double excitations from each low-energy configuration were considered. Since this led to over a million configurations, the perturbation scheme reported previously[10] was adopted. In this scheme, partitioning perturbation theory is used to write an effective Hamiltonian

$$\mathbf{H}_{eff}\mathbf{c}^0 = E\mathbf{c}^0 \tag{1}$$

where

$$\mathbf{H}_{eff} = \mathbf{H}^0 + \mathbf{h}^T(E\mathbf{1} - \mathbf{H}')^{-1}\mathbf{h} \tag{2}$$

If $\mathbf{H}^0$ contains the dominant configurations of the first few states and $\mathbf{H}'$ the less important configurations, then the correction to $\mathbf{H}^0$ will be small. In this case a fair approximation can be obtained by replacing $\mathbf{H}'$ by its diagonal elements $\mathbf{D}$ and $(E\mathbf{1} - \mathbf{H}')^{-1}$ by

$$(E\mathbf{1} - \mathbf{H}')^{-1} = (E_0\mathbf{1} - \mathbf{D})^{-1} + \Delta(E_0\mathbf{1} - \mathbf{D})^{-2}$$

where

$$\Delta = E - E_0$$

This gives

$$\mathbf{H}\mathbf{c}^0 = \Delta\mathbf{S}\mathbf{c}^0 \tag{3}$$

where

$$\mathbf{H} = \mathbf{H}^0 + \mathbf{h}^T(E_0\mathbf{1} - \mathbf{D})^{-1}\mathbf{h} \tag{4}$$

and

$$\mathbf{S} = \mathbf{1} + \mathbf{h}^T(E_0\mathbf{1} - \mathbf{D})^{-2}\mathbf{h} \tag{5}$$

The solution $E = E_0 + \Delta(E_0)$ to (3) depends only weakly on E_0, so one can readily interpolate to $E = E_0$. These points are then exact solutions to the CI problem with $\mathbf{H}'$ replaced by $\mathbf{D}$.

Table I. Molecular Properties of N-Methylacetamide (au)

	Ground state	$^1n\pi^*$	$^3n\pi^*$	$^3\pi\pi^*$
$\|\mu\|^a$	1.81	0.97	0.92	1.43
$\theta,^b$ deg	41	38	39	17
$Q_{yz}{}^c$	1.139	0.343	0.324	−0.161
Q_{xx}	−23.847	−25.073	−25.105	−24.208
Q_{yy}	−25.537	−24.043	−23.904	−24.294
Q_{zz}	−20.241	−20.674	−20.673	−21.486

^{a} Magnitude of dipole moment. ^{b} Angle of dipole moment with C–N bond, defined in Figure 1. $^c Q_{\alpha\beta} = \sum_B Z_B(r_B)_\alpha(r_B)_\beta - \langle\Psi|\sum_i(r_i)_\alpha(r_i)_\beta|\Psi\rangle$. All distances are measured from center of mass.

Table II. Excitation Energies of N-Methylacetamide Estimated by SCF and Cl Methods (eV)

state	frozen orbital	ΔE_{SCF}	ΔE_{Cl}	$\Delta E_{Cl}{}^{extrap\ a}$	exptl
$^3n\pi^*$	7.07	4.38	5.01^d	5.61^d	
$^3\pi\pi^*$	7.11	4.99	5.58^e	6.11^e	
$^1n\pi^*$	7.57	4.63	5.25^d	5.85^d	~5.5^b
$^2A'$	11.17	7.92	9.08^f	10 11^f	9.85^c
$^2A''$	10.60	8.88	9.19^f	9.66^f	9.68^c

^{a} Perturbation theory extrapolation for all double excitations. ^{b} See ref 6 and 9. ^{c} See ref 7. ^{d} Based on $^3n\pi^*$ orbitals. ^{e} Based on $^3\pi\pi^*$ orbitals. ^{f} Based on ground-state orbitals.

For the $^1A'$ states, 14 configurations were included in $\mathbf{H}^0$. These were the ground state, $\pi\pi^*$, n3s, n3p$_y$, n3p$_z$, n3d$_{yz}$, n3d$_{y^2-z^2}$, n3d$_{x^2}$, n4s, π3p$_x$, π3d$_{xz}$, π3d$_{xy}$, $\pi_2\pi_4 \rightarrow (\pi^*)^2$, and $\pi_3\pi_4 \rightarrow (\pi^*)^2$. All configurations connected to these configurations by matrix elements greater than 10^{-6} au in magnitude were included. This typically involved over 10^5 configurations for each configuration in $\mathbf{H}^0$.

Results

The ground-state SCF calculation gave an energy of −246.9403 au. All single excitations and the 1355 most important double excitations, as selected by perturbation theory, were used to produce 3332 spin-adapted configurations. The Cl energy was −247.1220 au and the coefficient of the SCF configuration was 0.96. Perturbation theory predicted a −0.226 au energy contribution compared to the −0.182 au actually obtained. Assuming all other configurations contribute in the same ratio, the extrapolated valence-shell double-excitation limit is −247.289 au. Snyder has pointed out that the correlation energy of closed-shell systems is nearly additive.[16] On this basis, the correlation energy of NMA should be the sum of that of formamide (−0.87 au) and ethylene (−0.68 au), or −1.5 au. The 60 MO's used here could give only about 22% of this. Approximately 8% more could come from higher excitations. The relatively small fraction of the correlation energy

accounted for here is a result of omission of polarization functions and truncation of the MO set.

Some molecular properties are reported in Table I. The ground-state dipole moment was 4.6 D rotated 41° from the C–N bond toward the oxygen atom (polarized C^+O^-). This is a typical result for amides.[8,17]

Table II summarizes some estimated excitation energies. Because relaxation effects exceed differences in correlation energy, parent-configuration SCF results are significantly better than single-configuration estimates using ground-state orbitals.

The $^1n\pi^*$ one-configuration energy using $^3n\pi^*$ orbitals was only 0.0015 au above its SCF energy. Hence, the use of the $^3n\pi^*$ orbitals for Cl calculations on both states seemed reasonable. At all levels of calculation the $^1n\pi^*-^3n\pi^*$ energy difference was predicted to be about 0.2 eV. This is about 0.1 eV less than found in formamide. On the basis of an experimental estimate[9] of 5.5 eV for the $^1n\pi^*$ state, the $^3n\pi^*$ vertical excitation energy should be 5.3 eV. The difference in procedures for selecting the virtual orbital basis for the ground and $^1n\pi^*$ states, as well as the low fraction of correlation energy recovered and lack of polarization functions, leads to a larger uncertainty in the calculation than obtained for formamide.

The parent-configuration SCF calculation for the $^3\pi\pi^*$ state gave a ΔE_{SCF} of 4.99 eV. At every level of calculation the $^3\pi\pi^*$ state was about 0.5 eV above $^3n\pi^*$ so its actual energy should be 5.8 eV. It will be noted that all three of the states discussed so far lead to essentially the same energy as formamide.

The experimental ionization energies of NMA are 9.85 ($^2A'$) and 9.68 ($^2A''$) eV. Koopman's theorem gives 11.17 and 10.60 eV, respectively, while Cl with ground-state orbitals gives 10.1 and 9.7 eV.

The perturbation results for the $^1A'$ states are summarized in Table III. Term values and oscillator strengths are also shown. These oscillator strengths are based on the zero'th-order configurations only and ignore contributions from higher configurations. The term values for the Rydberg states are reasonable. For example, the states which terminate in a 3p orbital have term values ranging from 21 600 to 23 200 cm^{-1}, which is near the value of 20 000 cm^{-1} expected for 3p states. The $^1\pi\pi^*$ state, on the other hand, is clearly at too high an energy, as the spectrum does not show a large oscillator strength near 8.2 eV. Furthermore, the spectrum has a much greater intensity near 7 eV than the calculation predicts.

Discussion

Our results clearly indicate that the $^3\pi\pi^*$ state lies about 0.5 eV above $^3n\pi^*$ at the ground-state geometry. On the basis of the lack of phosphorescence, McGlynn has concluded that the lowest triplet state is $^3\pi\pi^*$ in both NMA and formamide. These conclusions are not incompatible, however, since phosphorescence would occur from the excited-state equilibrium geometry. Larger geometrical changes are expected in the

Table III. Results of the Perturbation Theory Calculation on the $^1A'$ States of N-Methylacetamide

state	energy, au	ΔE, eV	oscillator strength	term value, cm^{-1}
ground state	−247.296			
n3s	−247.081	5.83	0.010	31 000
n3p	−247.046	6.80	0.015	23 200
n3p	−247.039	7.00	0.037	21 600
π3p	−247.034	7.13	0.046	22 000
n3d	−247.028	7.29	0.004	19 300
n3d	−247.025	7.37	0.015	18 600
n3d	−247.019	7.53	0.0005	17 300
n4s	−247.009	7.81	0.011	15 100
π3d	−247.005	7.93	0.029	15 500
π3d	−247.001	8.02	0.031	14 700
$\pi\pi^*$	−246.995	8.19	0.167	13 400
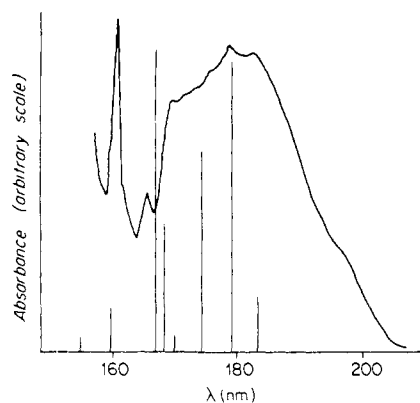
Figure 2. Experimental and model spectrum for *N*-methylacetamide (experimental spectrum from ref 5).

Table IV. Model Calculation on the $^1A'$ States[a]

dominant config	ΔE, eV	oscillator strength	dominant conf	ΔE, eV	oscillator strength
n3s	5.78	0.010	$\pi\pi^*$	7.41	0.096
n3p	6.78	0.017	n3d	7.54	0.0003
n3p	6.93	0.092	n4s	7.82	0.013
π3p	7.11	0.064	π3d	7.95	0.0002
n3d	7.28	0.004	π3d	8.06	0.004
n3d	7.36	0.040			

[a] Same as Table III, except that the $^1\pi\pi^*$ diagonal element has been lowered 1.0 eV.

$^3\pi\pi^*$ state than in the $^3n\pi^*$ state, and this could reverse their relative energy.

We do not believe that the $^3\pi\pi^*$ state can lie as low as 4.5 eV vertically above the ground state as McGlynn has conjectured although the T_0 value may well be this low. Part of his conjecture, however, is based on the assumption that the V_1 band is purely $^1\pi\pi^*$. Our calculations, while not very accurate, indicate this is not true.

Methylation of formamide lowers the ionization energy.[7] As a consequence, the Rydberg states lie lower in NMA than in formamide. This gives rise, among other things, to our difficulties in finding an SCF description for the $^1\pi\pi^*$ state. The V_1 band of amides changes shape and energy upon methylation. Examination of the spectra, however, indicates that part of the band remains near 7.3 eV, while a second component shifts to lower energy. In NMA this results in a rather flat peak with maxima extending from 7.3 to 6.8 eV.

Our calculations indicate that the $^1\pi\pi^*$ configuration is nearly unchanged in energy by methylation, while the n → Rydberg configurations are strongly shifted. This is plausible as the methyl groups destabilize the pπ orbitals on carbon and nitrogen and, hence, destabilize both π and π^*. Unfortunately, because of the large relaxation effects and correlation effects in the $^1\pi\pi^*$ configuration (discussed in our previous work on formamide[10]), our calculations seem to have left this configuration at somewhat too high an energy in H_{eff}. Consequently the oscillator strength distribution given in Table III does not match the spectrum. Conventional CI, even with one iteration to natural orbitals within the truncated IVO basis, did not lower the $^1\pi\pi^*$ state.

To test our ability to model the spectrum, we have carried out a calculation with the $^1\pi\pi^*$ diagonal element of H_{eff} artificially lowered by 1.0 eV. Table IV and Figure 2 give the results for this model calculation. This gives a spectrum with an oscillator strength distribution closely resembling the experimental one. Of course, the states labeled as ^{1}n3p, $^1\pi$3p, and $^1\pi\pi^*$ all draw their large oscillator strengths from an admixture of the $^1\pi\pi^*$ configuration. In our opinion, this is close to a true description of the $^1A'$ states of NMA, although all of the states in Figure 2 seem to be high by 0.1 eV.

This interpretation explains why the $^3\pi\pi^*$ energy is nearly

unchanged between NMA and formamide, while the V_1 band edge is shifted. Participation of the ^{1}n3p configuration in the V_1 band is, of course, well-known from formaldehyde[18] and hence not unexpected.

Ab initio theory has now demonstrated in a variety of molecules that V bands are not *simply* $^1\pi\pi^*$ transitions. Rather, strong mixing with Rydberg states is a common feature. In amides, this zero'th-order mixing between valence and Rydberg states is strongly perturbed by methylation. This leads to quite different band shapes in different molecules, including, possibly, the splitting of the $^1\pi\pi^*$ intensity into two distinct bands in *N,N*-dimethylacetamide.

In our opinion, the past attempts[9] to interpret the changes produced by methylation in terms of shifts in a purely valence state are seriously misleading. The true situation is much more complex than implied by such a simple approach. The $^3\pi\pi^*$ state does not suffer from these complications, since it lies below the triplet Rydberg levels and is primarily a carbonyl excitation.

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